

DEVELOPMENT OF OFFGAS SAMPLE COLLECTION METHODS FOR AN EMISSIONS INVENTORY OF A HIGHLY ACIDIC RADIOACTIVE WASTE THERMAL TREATMENT PROCESS

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ABSTRACT

A cooperative effort between the US Department of Energy (DOE), regulatory, facility operations, and subcontractor organizations has applied EPA sampling and analysis methods to measure air emissions from a highly radioactive waste calcination process that produces a highly acidic, humid offgas.

The New Waste Calcining Facility (NWCF) located at the Idaho National Engineering Laboratory (INEEL) uses a calciner to convert highly radioactive liquid wastes stored in the Idaho Nuclear Technology and Engineering Center (INTEC) tank farm into a dry granular calcine for volume reduction and safer temporary storage. Calcination of the nitric acid wastes produces offgas that contains elevated levels of NO_x, which is mainly NO₂. The offgas also includes evaporated water from the liquid waste and products of combustion from in-bed combustion of kerosene that is used to provide bed heating. Measurements of Calciner offgas emissions have been determined to be necessary to verify assumptions used in site-specific risk assessment calculations.

The high NO_x levels have been found to interfere with the standard EPA volatile organic compound (VOC) and semivolatile organic compound (SVOC) sampling and analysis procedures. A three-phase program has been conducted to adapt and demonstrate the EPA-SW-846 methods for monitoring organic and metals emissions from the Calciner. This program was devised in collaboration with the State of Idaho Department of Environmental Quality, EPA Region 10, EPA Office of Research and Development, and subcontractors. This collaboration was obtained with the help of the EPA/DOE National Technical Workgroup for Mixed Waste Treatment. Phase I (bench-scale) and Phase II (pilot-scale) tests indicated that the methods can be adapted to mitigate the interference problems.

Phase III was a field demonstration on the Calciner system of sampling/analysis method adaptations identified in Phases I-II. Given the successful demonstration of the sampling and analysis methods, Phase III also included the performance of an emissions inventory for the Calciner. Three different test series were conducted during February-April 1999. The testing was funded by DOE, directed by INEEL, and performed by INEEL and subcontractors (Science Applications International Corporation and Quanterra Incorporated). The scope of testing included:

- Monitoring and control of Calciner system operating conditions within generally typical ranges, at two different Calciner operating temperatures of 500° C and 600° C
- Manual offgas sampling and analysis for particulate matter (PM), HCl, Cl₂, selected metals including Hg, volatile organic compounds (VOCs), dioxins and furans (D/Fs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), other semi-volatile organic compounds (SVOCs), and total organics (TO)
- Offgas continuous emissions monitoring for gaseous species O₂, CO₂, CO, NO, NO₂, HCl, and total hydrocarbons (THC)
- Sample collection and analysis of the waste feed, scrub solution, calcine product, and condensate.

The test program resulted in (a) test method adaptations to minimize NO_x interference during sampling and analysis, (b) development of procedures to mitigate radioactivity and industrial hygiene hazards during all phases of sample collection, sample shipping, and analysis, and (c) unprecedented measurements of offgas emissions from the Calciner process.

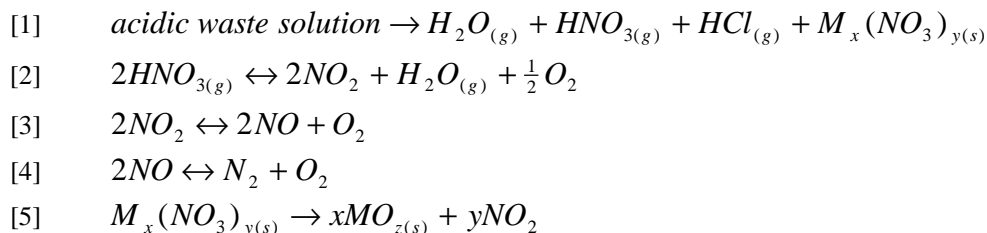
INTRODUCTION

The Idaho National Engineering and Environmental Laboratory (INEEL) is located in southeastern Idaho along the edge of the Snake River Plains. It is currently managed and operated by Lockheed Martin Idaho Technologies Company (LMITCO), a consortium of companies under contract to the U.S. Department of Energy (DOE). The INEEL consists of several facilities, including the Idaho Nuclear Technology and Engineering Center (INTEC). Up until 1992, one of INTEC's missions was to reprocess nuclear fuels by dissolving the fuels and then separating uranium from the fission products in the dissolver solution. The radioactive acidic wastes were stored in stainless steel tanks prior to being thermally converted into a dry, granular, free-flowing solid, using a process referred to as waste calcination. This process prevents the accumulation of vast amounts of radioactive liquids by converting these liquids into a solid form that is safer for temporary storage.

Waste Calcination Process

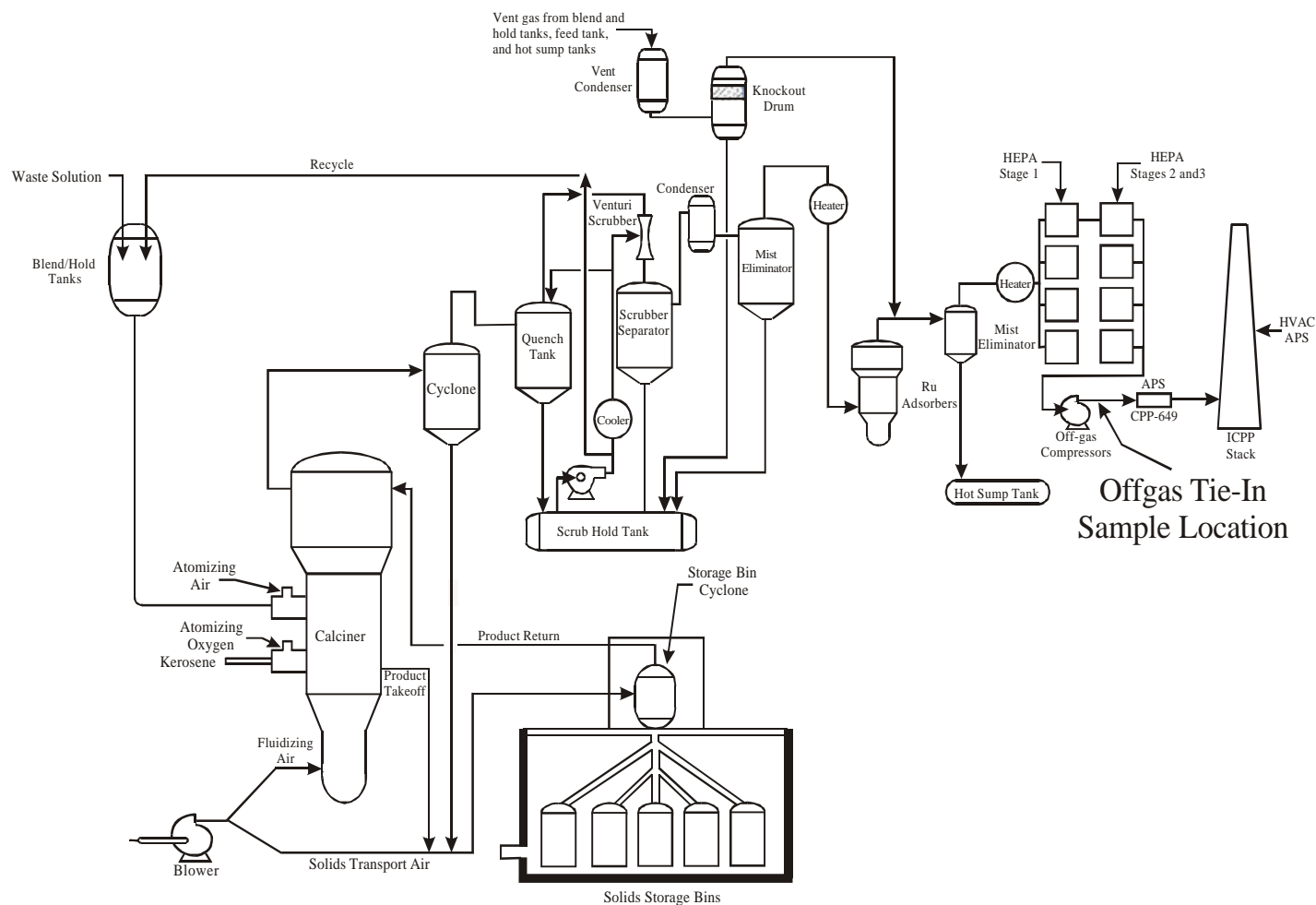
The waste is calcined by spraying the acidic liquid into an air-fluidized bed of heated spherical dolomite particles. The waste droplets impinge on the bed where the liquid evaporates and the residual salts are subsequently converted to solid metal oxides that add to the particles in the bed. As the amount of solid bed material increases, the particles are drained from the calcining vessel and pneumatically transported to storage bins. The bed is eventually composed entirely of particles created by the dried feed. This product is referred to as calcine.

The following set of global reactions describe the chemical transformation of the constituents in the feed to calcine.



Where, M represents a given metallic element in the waste feed. The forward and reverse rates of Equations 3 and 4 are relatively slow at conditions in the Calciner. Both theoretical calculations and measurements indicate that less than 5 mole percent of the total nitrate in the waste feed is converted to molecular nitrogen and oxygen.

Calcination was initially demonstrated in the INTEC Waste Calcining Facility (WCF) using indirect heating with molten Na-K metal. This facility was replaced by the New Waste Calcining Facility (NWCF) in the early 1980's (1). Figure 1 shows a schematic of the NWCF calcination process. The calciner vessel has a 5-foot diameter bed section and an 8 ft diameter particle disengaging section, which together give the calciner a total height of 15 ft. The calciner is heated using in-bed combustion of kerosene fuel, sprayed into the bed through separate fuel nozzles. Pure oxygen is used to atomize and burn the kerosene to achieve efficient combustion and efficient heat transfer to the bed. The design bed operating temperature ranges from 380 to 650°C, although the bed has been typically operated at 500°C.



NWCF Process wo.cdr

Figure 1. Calciner process schematic.

The Calciner offgas treatment system removes calcine fines and radioactive species from the offgas with the high efficiency required to meet radioactivity emission regulations. A hot cyclone separator removes much of the calcine fines from the offgas. The offgas is then rapidly cooled to its dewpoint in a quench tower, and a venturi scrubber removes much of the remaining entrained fines. The scrub solution used in the quench tower and the scrubber contains 3-4 M nitric acid so fines are dissolved into solution. Aerosols from the venturi scrubber are removed in the scrubber separator and demister. The silica bed adsorbers, originally designed to capture ruthenium, serve as a prefilter for triple-stage high efficiency particulate (HEPA) filters. The offgas is reheated upstream of the HEPA filters. Offgas compressors induce a negative pressure of around 40 in. H₂O on the Calciner, and maintain a pressure drop of up to 60-70 in. H₂O across the venturi scrubber. The compressors vent the offgas to an Atmospheric Protection System (APS), where the offgas is combined with additional process vent offgas, further HEPA filtered, and then combined with building ventilation air as it is vented through the INTEC main stack. Continuous monitors for NO_x and radioactive emissions are located at the stack.

An example composition of the liquid waste currently being treated by the Calciner is given in Table 1. The high nitrate concentration in the waste produces offgas that contains elevated levels (up to 30,000 ppmv) of NO_x, which is mainly NO₂. This is in contrast to typical NO_x levels of less than 1,000 ppmv for most combustion

processes, in which the majority (~90-95%) of the total NO_x is NO. The waste also contains several hazardous metals and a variety of radionuclides. While much of the hazardous metals and radionuclides are retained in the calcine at the relatively low calcine temperature, constituents that appreciably partition to the offgas include Hg and tritium (H-3).

TABLE I
Average Composition of INTEC Sodium-Bearing Radioactive Liquid Wastes (1, 2).

Non-Radioactive Constituents			Radionuclides		
Species (Ion)	Units	Amount	Species	Units	Amount
Specific gravity	g/cm ³	1.30	H-3	mCi/L	0.02 ^δ
Acid (H ⁺)	M	1.59	Sr-90	Ci/m ³	38
Nitrate (NO ₃)	M	5.07	Cs-134	Ci/m ³	1.1
Fluoride (F)	M	0.070	Cs-137	Ci/m ³	41
Chloride (Cl)	M	0.038	Pu-238	nCi/m ³	245
Sulfate (SO ₄)	M	0.055	Pu-239	nCi/m ³	35
Phosphate (PO ₄)	M	0.014	Am-241	nCi/m ³	90
Aluminum (Al)	M	0.69	U	g/L	0.12
Sodium (Na)	M	1.9	^δ Estimated concentration		
Potassium (K)	M	0.15			
Calcium (Ca)	M	0.054			
Boron (B)	M	0.018			
Iron (Fe)	M	0.022			
Zirconium (Zr)	M	0.002			
Molybdenum (Mo)	M	0.0006			
Manganese (Mg)	M	0.013			
Cadmium (Cd)	M	0.003			
Chromium (Cr)	M	0.004			
Mercury (Hg)	M	0.0011			
Lead (Pb)	M	0.0012			

One shortcoming of in-bed combustion is the potential generation of incomplete products of combustion. Although the majority of the fuel is efficiently burned in the flame zone created by the high momentum fuel nozzles, a small fraction of the atomized kerosene impinges on the calcine particles where it is volatilized and burned in the relatively cooler bed. Consequently, not all of the fuel is completely combusted, as indicated by an offgas stream containing upwards of 1 volume percent CO (10,000 ppmv).

NWCF Permitting

The liquid wastes stored at the INTEC Tank Farm Facility are categorized as mixed radioactive-hazardous wastes. A Court-Order Settlement Agreement with the State of Idaho requires DOE to cease use of these tanks under specific conditions by 2012. An Environmental Impact Statement is being prepared to help determine how to best accomplish this commitment. Continued use of the Calciner is one option that is being considered. The ability to operate the Calciner under current environmental regulations is a prime consideration.

The Calciner is presently operating under a Consent Order with the State of Idaho under commitments which include offgas sampling to support DOE's decision whether DOE will attempt to meet Idaho's designated performance standards for this facility and the proposed Maximum Achievable Control Technology standards (3). NWCF emissions measurements are thus necessary to provide data to make decisions regarding management of the stored liquid wastes.

Prior Test Method Evaluations

In 1991-92, Radian Corporation (now Eastern Research Group) was contracted to investigate the applicability of EPA test methods for the NWCF. They conducted a laboratory study to demonstrate the feasibility of using standard EPA sampling and analysis methods for measuring emissions of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in the high NO_x offgas. Radian identified significant problems with the standard VOC and SVOC sampling trains and sample analysis methods when attempts were made to sample in the presence of the high NO_x concentrations. Laboratory-blended simulated calciner offgas, containing around 20,000 ppmv NO₂, oxidized both the VOC and SVOC analytes and the organic resin sorbents used to collect the samples. Reactions with the analytes resulted in erroneous measurements, while severe oxidation, or even ignition, of the resin sorbents occurred in some instances. The high levels of NO₂ also caused significant corrosion and increased maintenance requirements of the laboratory analysis equipment. Technical problems were even noted when the simulated calciner offgas was diluted with air to lower the NO₂ concentration to levels observed in the INTEC main stack (~500 ppmv), after the NWCF offgas is diluted by a factor of around 60 times.

Caustic scrubbing to remove NO_x upstream of the sorbent cartridges was also evaluated. The up-front scrubbing successfully preserved the sorbent from excessive oxidation; however, erroneous results were still observed, due (at least in part) to reactions of some of the VOC and SVOC analytes in the caustic scrub. Radian recommended that stream dilution, and possibly a combination of stream dilution and up-front caustic scrubbing could improve the sample collection results.

LABORATORY AND PILOT PLANT TESTS

Follow-on research was initiated at INEEL in 1997 to investigate whether the standard EPA sampling methods could be used to sample the Calciner offgas, and to determine if any potential enhancements to the sample collection and analysis methods would improve the sampling results. A workshop sponsored by the National Technical Workgroup for Mixed Waste Treatment (NTW) was held in May 1998 to review the previous studies and to consider possible modifications to mitigate NO_x interference. The workshop included representatives from the State of Idaho Department of Environmental Quality (DEQ), EPA Region 10, DOE Idaho Field Office, the EPA Office of Research & Development (ORD), and private industry consultants. Recommendations included one, or a combination of, the following techniques: (a) dilution of the concentrated stream, (b) rinsing the sorbents during or immediately following sample collection, (c) preventing acidic moisture condensation from occurring on the sorbents by maintaining the sample gas temperature above its dewpoint, and (d) placing a caustic or neutral impinger upstream of the sorbent cartridge to scrub the acidic components prior to contact with the sorbent. The scope of sampling and analysis was expanded to include measurements for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (D/Fs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated bi-phenyls (PCBs), other SVOCs, VOCs, and metals.

With recommendations from the NTW workshop, a test plan was developed to demonstrate the EPA-SW-846 methods for monitoring organic and metals emissions from the NWCF (4). Phase I (laboratory) and Phase II (pilot plant calciner) tests were conducted to demonstrate test methods and modifications using non-radioactive gas. The laboratory tests were conducted using a simulated offgas produced in a bench-scale evaporator system. The pilot-scale tests were conducted using an INTEC pilot-scale research calciner facility designed to model the NWCF Calciner.

Test Matrix and Equipment

The test matrix included Method 0030 (Volatile Organic Sampling Train or VOST) and modified Method 0023A sampling and analysis to evaluate the recommendations of the NTW workshop. Sample gas NO_x levels were varied from less than 200 ppm to 20,000 ppm for different sample procedure modifications. Non-

isotopically-labeled VOCs were dynamically spiked into the acidic gas, and non-labeled SVOC matrix spikes were added to the XAD-2 resins, to simulate native organic compound emissions.

Laboratory tests using laboratory-generated simulated offgas were followed by tests on actual offgas produced from the INTEC 10-cm internal diameter pilot plant calciner facility. The 10-cm calciner simulates the actual Calciner, and produces an offgas similar to the actual Calciner offgas. The pilot plant is equipped an offgas cyclone and venturi scrubber for particulate removal. Hence, the pilot plant tests also served as an initial indicator of the types of hazardous pollutants that could possibly be formed in the NWCF without the associated radiological constraints that exist with the actual Calciner offgas.

Laboratory and Pilot Plant Test Results

The laboratory tests confirmed earlier results which indicated NO_x interference using the standard EPA SVOC and VOC sampling and analysis procedures. As suspected, the synthetic offgas was especially harsh, causing resin degradation and even oxidation in some cases. Surrogate recoveries were poor, which was attributed to higher partial pressures of nitric acid that were produced by inefficient conversion of the acid vapors to NO₂ and NO.

The pilot plant results, on the other hand, revealed that valid results were possible at various NO_x concentrations up to 20,000 ppm. Surrogate recovery results for the pilot plant tests are shown in Table II. Results are summarized as follows:

- Acceptable or excellent surrogate recoveries were obtained for the D/F and PCB measurements, regardless of standard or modified sample train configurations, for NO_x levels up to 1,000 ppm. This good performance was attributed to the compound specificity of these procedures and the extensive laboratory sample preparation and cleanup procedures. D/F and PCB measurements were not made with NO_x levels above 1,000 ppm.
- Acceptable or excellent surrogate recoveries were generally obtained for the VOC measurements, except for a single measurement made at 20,000 ppm NO_x and a single measurement with the train configured to prevent acidic condensation in the Tenax sorbent.
- Acceptable or excellent surrogate recoveries were generally obtained for the SVOC measurements, except for a single up-front caustic scrubbing measurement made with 400 ppm NO_x.
- PAH surrogate recovery results were generally worse than for the other organics. This poorer performance was probably due to the use of deuterated recovery standards, which tended to exchange their deuterium with hydrogen in the acidic sample matrices.

The following recommendations for additional testing resulted from the bench and pilot-scale tests:

- Sample gas dilution to as low as 1,000 ppm and post-sample-collection rinsing/neutralization can reduce NO_x interference. However, it is still not clear if the reduced interference is due to lower NO_x concentrations or to lower sample gas volumes.
- Rinsing of the sorbent traps for the 0010, 0023A, 0030, and 0031 sample trains is necessary to minimize NO_x interactions with the sorbent resins and with analytes adsorbed on the resins. XAD-2 resin should be rinsed with NaOH solution to neutralize the acidity. VOC sorbent resin should be rinsed with organic-free water rather than caustic solution, to minimize the potential to destroy VOCs in the caustic solution.
- Rinse solutions and impinger catches should be carefully titrated prior to shipment for laboratory analysis to neutralize any residual acidity without resulting in excessive basicity.
- Other sample procedure modifications that were evaluated (up-front caustic scrubbing and noncondensing train operation) do not significantly improve performance, and represent greater departures from the standard procedures.

TABLE II

Sample collection quality indicators for the pilot plant sampling tests.

Train Configuration	Test No.	NO _x (ppm)	Internal Standards Recovery			Lab or Sampling Surrogate Recovery			Sampling Surrogate Recovery (%)
			Excellent	Acceptable	Poor	Excellent	Acceptable	Poor	
VOST Standard Train with Offgas Dilution	II-40	200	3			4			
	II-39	400	3			4			
	II-38	1,000	3			NA	NA	NA	
VOST Non-condensing Offgas	II-44	400	3			4			
	II-43	1,000			3			4	
VOST Neutral Continuous Rinse	II-50	400	3			4			
	II-49	1,000	3			3	1		
	II-48	20,000		1	2		1	3	
VOST Up-front neutral scrub	II-54	400	3			4			
VOST Up-front Caustic Scrubber	II-53	400	2	1		2	1	1	
	II-55	1,000	3			3	1	1	
SVOC Standard Train with Offgas Dilution	II-37	200	6			5	1		110
	II-35	400	5	1		5	1		119
	II-33	1,000	6			4	2		100
SVOC Non-condensing Offgas	II-42	400	6			3		3	120
	II-41	1,000	6			6			109
SVOC Caustic Continuous Rinse	II-47	400	5		1	3		3	112
	II-46	1,000	6			4		2	107
	II-45	20,000	6			3		3	126
SVOC Up-front Caustic Scrubber	II-51	400	6			5		1	96
	II-52	1,000	6			5	1		-
PAH Standard Train with Offgas Dilution	II-37	200	12	4		1	1		
	II-35	400	12		4	1	1		
	II-33	1,000	12	4		1			
PAH Non-condensing Offgas	II-42	400	12	2	2	2			
	II-41	1,000	15	1		2			
PAH Caustic Continuous Rinse	II-47	400	10	4	2	2			
	II-46	1,000	11	4	1				
	II-45	20,000	2	2	12			2	
PAH Up-front Caustic Scrubber	II-51	400	15	1		1	1		
	II-52	1,000	11	4	1	1	1		
D/F Standard Train with Offgas Dilution	II-36	200	9			4	1		
	II-56	400	9			4	1		
	II-34	1,000	1	8		3	2		
D/F Non-condensing Offgas	II-20	1,000	9			5			
D/F Neutral Cont. Rinse	II-24	400	9			5			
D/F Caustic Cont. Rinse	II-26	400	9			5			
D/F Up-front Caustic Scrub	II-29	400	9			NA	NA	NA	
PCBs Standard Train with Offgas Dilution	II-36	400	8	2			1		
	II-56	400	7	2		1			
	II-34	1,000	7	2		1			
<div> <div>Evaluation Criteria</div> <div> Excellent Acceptable Poor </div> </div> <div> <div>Internal Standards (φ)</div> <div> 75% ≤ φ ≤ 150% 50% ≤ φ 75% (or) 150% < φ ≤ 200% φ < 50% (or) 200% < φ </div> </div> <div> <div>Lab or Sampling Surrogates (φ)</div> <div> 75% ≤ φ ≤ 125% 50% ≤ φ < 75% (or) 125% < φ ≤ 150% φ < 50% (or) 150% < φ </div> </div>									

- Further evaluation of the improved method techniques is needed with actual offgas at NO_x levels above 1,000 ppm. Good surrogate recoveries may be possible at higher NO_x levels. Measurements on the actual Calciner offgas appear to be feasible and ready for demonstration.
- Following initial parametric tests for D/F, PCB, PAH, and SVOC analyses all made from the same sample train, separate trains should be used for combined D/F and PCB (modified 0023A), PAH (0010), and SVOC

(0010) measurements. Making these measurements in three separate trains can improve detection limits, eliminate incompatibilities between sampling surrogates for the low-resolution and high resolution analytical procedures, and eliminate incompatibilities in sample recovery solutions.

- The PAH procedure should be modified to replace the deuterated surrogates with C-13 labeled surrogates.

PHASE III TEST PROGRAM

Phase III, which is currently in progress, includes (a) evaluation of the feasibility of using sampling/analysis methods demonstrated in Phases I-II for measuring actual NWCF emissions, and (b) performance of an emissions inventory of the NWCF, given that the sampling/analysis methods are successfully demonstrated with actual Calcliner offgas.

Project Organization

The project team included personnel from many different organizations and disciplines. LMITCO engineers and technicians planned and directed the emissions inventory testing, assured that the testing was safe and consistent with current LMITCO and DOE procedures, and ensured that the test results were as valid as technically feasible given that many of the sampling and analysis procedures were modified to enable safe sample collection of the radioactive and hazardous offgas and to mitigate the affects of high levels of NO_x on sample collection and analysis. Different LMITCO organizations represented on the project team included the High Level Waste Program, Advanced Engineering and Development Laboratory, Quality Assurance & Oversight, Operations, Engineering, Radiological Control, Industrial Safety, Industrial Hygiene, Sample Management Office, Environmental Affairs, INTEC Services (Directives and Requirements, Operations Procedure Writers, Change Control), Packaging and Transportation, Waste Generator Services, and Field Projects.

Field sampling was performed by Science Application International Corporation (SAIC) under subcontract to LMITCO. SAIC provided most of the manual sampling equipment and supported test planning. Sample analysis was performed by Quanterra Incorporated under contract to SAIC. Project planning and review was also provided by the NTW-sponsored workgroup of Idaho DEQ, EPA Region 10, EPA ORD, and subcontracted personnel addition to LMITCO, SAIC, and Quanterra personnel.

Planning and Work Control for Safe Sampling and Data Quality

Several adaptations to standard test methods were required to mitigate both radiological risks and exposure to hazardous gas atmospheres and to ensure adequate data quality. The arecommendations from the bench and pilot-scale tests were implemented. Implementation of these recommendations and other adaptations were defined by plans and work control procedures that were developed by this project. These work control plans and procedures were required by DOE, LMITCO, and INTEC:

- A test plan (5) that defined test objectives, test matrix, project organization, test methods, and schedule
- A quality assurance project plan (6), that conformed to DOE orders and EPA guidance for environmental monitoring/sampling projects and addresses data quality objectives and how those objectives will be met
- Work control procedure documents (7, 8, and 9) that define performance of operations; how the work will be coordinated with INTEC Operations, Industrial Safety and Hygiene, Waste Generator Services, Sample Management, sample contamination screening, sample shipping, and other support services; and personnel training requirements
- Safe work permits that identified potential hazards, monitoring, and personal protective equipment needed for the sampling activities

- Procedures that define responses to potential emergency situations such as loss of contamination control, power outages, and compressed gas leaks

A safety analysis plan was developed with involvement of LMITCO Radiological Controls Engineering, Industrial Safety & Hygiene, and Waste Generator Services, among other company service organizations. The technical procedures included step-by-step instructions to perform such tasks as inserting and manipulating the sample probes and operating the sample collection trains and continuous gas emissions monitor (CEM). This level of detail was mandated by INEEL work control requirements to assure that work with associated radiological and industrial hygiene hazards was done safely.

Sample team personnel received extensive safety training, which included Rad Worker II, chemical hygiene, and response to emergency conditions training. Personnel were required to wear full anti-contamination clothing and supplied-air during probe insertion and removal from the offgas access ports. Arm-length anti-contamination plastic gloves and latex outer gloves were required while operating the sample collection trains inside a contamination control hood. Continuous coverage by a radiological control technician and a health physicist was required to perform all sample collection and sample recovery.

Containment areas with administrative controls, monitoring, and HEPA-filtered contamination area hoods were designed to isolate potential contamination releases. A contamination control tent was placed over the sample location. A designated contamination area was located inside the tent immediately surrounding the sample ports. The tent also contained a contamination hood in which all sampling equipment was operated. All sample recovery was done in this hood or in a contamination hood located inside an adjacent trailer. Another adjacent trailer with radiological and industrial hygiene controls housed the continuous emissions monitoring system and the onsite gas chromatography laboratory. Continuous workplace air monitoring was performed in these work areas to assure that any releases of radioactivity, NO_x, CO, HCl, or flammable gases including hydrogen would be detected so that appropriate actions could be taken.

The sample ports were customized with dual shutoff valves, so that when no probe was in the port, there would be at least two levels of offgas containment (three levels with both valves closed and the port capped). The ports were also customized with purge air to maintain positive pressure on the annulus surrounding the sample probes. The ports and probes were also customized to allow for a compression fitting seal on the probe, so that when a probe was in a port, the port purge air and the seal around the probe provided two levels of offgas containment to prevent leakage through the port.

The modified Method 5-type sample trains were defined to begin at the back end of the sample probe. This was needed to enable the sample probe to routinely remain in place in the sample port, considerably reducing risk of radioactive and NO_x leaks, probe breakage, or exposure to workers. The sample probe was not leak-checked or recovered for each train. Leak-checks were conducted from a heated glass valve attached to the back end of the sample probe. The valve was required for contamination and NO_x control, and was not removed or recovered during the test series duration. The impact was considered small because (a) the probe was heated to 250°F, minimizing any condensation of materials onto the inner wall, (b) the probe was “conditioned” in the offgas prior to sample collection, and (c) the offgas is venturi-scrubbed, and triple HEPA filtered upstream of the sample location, removing all but very small sub-micron particulate matter (PM) that can more easily follow gas flow lines and avoid deposition on the inner wall.

The sample rate and duration for different trains was adjusted according to calculations to achieve the necessary detection limits for emissions that may drive the risk assessment, while minimizing interference of NO_x. With smaller sample volumes, the NO_x interference appeared to be less, and the need for sample gas dilution was reduced. Minimum sample gas volumes (with no dilution) were calculated to be 0.2 dscm for D/Fs, 0.1 dscm for PCBs, up to 0.1 dscm for several SVOCs and VOCs, and 0.05 dscm for benzo(a)pyrene. Target undiluted sample gas volumes were reduced to 0.75 dscm for 0010 (separate PAH, SVOC, and TCO) and 0023A (combined D/F and PCB) trains, and 5 liters per VOST set. The 0060 (multiple metals including Hg) trains were limited to 0.5 dscm because higher sample gas volumes depleted the acidified KMnO₄ Hg adsorbing solution. The sample volume for non-Hg 0060 sample trains was increased to 3 dscm to improve detection limits for the other metals. More standard sample volumes of 1 dscm were used for the 0050 (HCl and PM) train, and 30 liters for the 0040

(Field GC/FID) train. When diluted 0010 trains were run for PAHs and SVOCs, the total diluted sample gas volume was 3 dscfm, but the sample volume of actual sample gas was only 0.15 dscfm, at a dilution factor of 20.

Sample gas dilution and post-test rinsing were identified in bench and pilot-scale tests to minimize NO_x interference. Other sample train configuration and operation modifications that were evaluated did not sufficiently improve results, and were not included in current test planning. Test results showed that the sample gas may need to be diluted by a factor of 20x or more to lower total NO_x levels to 1,000 ppm or less. Adding dilution gas (N₂) to the sample gas caused low isokinetics of around 5%, and increased the propagated uncertainty in the sample gas volume measurement.

The dilution system used precision, factory-calibrated mass flow meters for accurate dilution N₂ metering, and also used a continuous O₂ meter to precisely measure the dilution factor for the sample gas. Error propagation calculations showed that the sample gas volume error could be as high as -48% to +28%. Calibrations done by directly measuring the sample gas flowrate, the dilution gas flowrate, the meter box total gas flowrate, and the dilution ratio showed that (a) the sample gas flowrate measurement error was within +/-10%, and (b) there was no detectable ambient air inleakage into the sample trains during operation. Presurvey and Test 1 results suggested that by using smaller sample volumes, lower sampling rates, prewetting the sorbents, post-sample rinsing of the sorbents, and post-sample titrations to neutralize acidic rinses and impinger catches, NO_x interference could be adequately mitigated so that sample gas dilution could be avoided on all organic trains except for (and possibly including) PAHs and SVOCs. For this reason, sample train dilution was ultimately used only on PAH and SVOC trains in Test Series 1, and undiluted PAH and SVOC sampling was performed in Test Series 1 through 3.

Sample Contamination Survey & Screening

Management Control Procedure MCP-1173 was developed to ensure that sample contamination levels would meet the sample acceptance criteria of the Quanterra laboratory radioactive materials license. During the Presurvey testing, representative samples for each type of the sample train were obtained and submitted to the INTEC radiochemistry laboratory for tritium analysis, gamma radiation scans, and gross alpha/beta particle emissions measurements. The results indicated that the contamination levels would safely meet the laboratory's acceptance criteria. The Presurvey sample results established a baseline for on-going sample contamination screening.

Each sample collection series began with a contamination screening train to confirm that contamination levels remained within the baseline. Because the radiological analyses destroyed the samples recovered from this train, these samples were not analyzed for emission measurements. During each test series following the initial sample contamination survey train, selected samples were periodically diverted for a non-invasive, extended quantitative gamma scan counting. Also, all samples were frisked for gamma radiation when they were removed from a contamination hood or from a radiological control buffer area. These multiple levels of radiological analyses prevented any worker exposure to contamination, assured that no contamination could be spread as the samples were handled, and that contamination levels in the samples were acceptable prior to shipment of samples to Quanterra for analysis.

Presurvey and Test Series

Calcliner offgas measurements were performed during a three-month period from February through April 1999. The scope of testing is summarized in Table III. This scope of testing was defined primarily by recent EPA guidance for emissions testing to support site-specific risk assessments (10). A dry run and three test series were conducted as follows:

TABLE III

Summary of Calciner emissions inventory measurements

Sample train procedure	Measurement	Train description	Analytical procedures
0010 (11)	SVOCs	Isokinetic traverse, glass-lined probe, heated filter, XAD-2 sorbent, impingers	3542/8270C GC/MS
0010 (10) / modified CARB 429 (12)	PAHs		8290 / Modified CARB 429 HRGC/HRMS
0010 (11)	TCO and GRAV		GC/FID (TCO), gravimetric analysis (GRAV)
0023A (11) / CARB 428 (12)	D/Fs and PCBs		8290 HRGC/HRMS (D/Fs and PCBs)
0060 (11)	Multiple metals including Hg	Isokinetic traverse, glass-lined probe, heated filter, sorbent, impingers	6010A (ICAP) or 7000 series (GFAAS) for multiple metals, 7470 (CVAAS) for Hg
0050 modified for PM (11)	HCl, Cl ₂ , PM		9056/9057 (IC for HCl and Cl ₂), Method 5 (gravimetric for PM)
0030 VOST (c) (Presurvey and Test Series 1)	VOCs	Single point, non-isokinetic, glass-lined probe, filter, Tenax/charcoal sorbents	5041A/8260 GC/MS
0031 (11) (Test Series 2 and 3)	VOCs including those with boiling point >30 °C	Single point, non-isokinetic, glass-lined probe, filter, 3 tubes – Tenax, Tenax, and Tenax/Anasorb	5041A/8260 GC/MS
0040 (11)	Field GC/ FID	Single point, nonisokinetic, glass-lined probe, filter, condensate analysis, bag sample analysis	0040 (Field GC/FID)
TO-14 (13)	VOCs	Evacuated Summa canister	GC/MS
3A, 7E, 10, 25A (14)	O ₂ , CO ₂ , NO, NO ₂ , CO, THC, HCl	CEMS: Single point, nonisokinetic, heated sample line, permeation dryer, offgas dilution	O ₂ , CO ₂ : 3A (paramagnetism and NDIR/GFC) NO, NO ₂ : 7E (NDIR/GFC, DUV) CO: 10 (NDIR/GFC) THC: 25A (hot FID) HCl: NDIR/GFC
<p>Multiple metals are the same 18 metals listed in the EPA guidance for emission measurements for supporting risk assessments (10). They include the 10 Method 0060 metals (As, Be, Cd, Cr, Ag, Ba, Hg, Pb, Sb, Tl) and also Al, Co, Cu, Mn, Ni, Se, V, and Zn.</p> <p>CVAAS = Cold vapor atomic absorption spectroscopy D/Fs = Dioxins and furans DUV = Dispersive ultraviolet FID = Flame ionization detection FGC = Field gas chromatography fraction of total organics, with boiling points less than 100 C GC/FID = Gas chromatography/flame ionization detector GC/MS = gas chromatography/mass spectrometry GFAAS = Graphite furnace atomic absorption spectroscopy GRAV = Nonvolatile, gravimetric fraction of total organics, with boiling points greater than 300 degrees C Hot FID = FID designed for hot THC without cooling the gas to remove moisture, and avoiding potential to remove some THCs HRGC/HRMS = High resolution gas chromatography/high resolution mass spectrometry IC = Ion chromatography ICAP = Inductively coupled argon plasma emission spectroscopy NDIR/GFC = Nondispersive infrared/gas filter correlation PAHs = Poly-cyclic aromatic hydrocarbons PCBs = Polychlorinated biphenyls PM = Particulate matter SVOCs = Semi-volatile Organic Compounds TCO = Total Condensable Organics, referring to total SVOCs with boiling points between 100-300 C THC = Total Hydrocarbons VOCs = Volatile Organic Compounds measured using the VOST procedure VOST = Volatile Organic Sampling Train</p>			

- Presurvey, February 8-11, 1999
- Test Series 1, February 25-27, and March 1-4
- Test Series 2, March 15-19
- Test Series 3, April 5-9 and April 12

The Presurvey was conducted to (a) provide initial data collection for assessing radiological and NO_x contamination and exposure hazards and assuring that those hazards are mitigated in subsequent testing, and (b) perform selected sampling procedures to validate work control procedures. The presurvey included sample collection using selected sample trains. The sample gas was not diluted in order to obtain conservatively high sample gas volumes and to verify the performance (lack of degradation or oxidation) of the sorbents used in those trains when exposed to the undiluted, high NO_x sample gas. The train samples were recovered for radiological assays to assess radioactivity levels in the samples.

The first attempt to collect a sample with XAD-2 resin had to be aborted only minutes into the test due to sudden and severe decomposition and charring of the resin. This did not occur during the pilot plant tests, possibly because moisture in the pilot plant offgas more rapidly wetted the resin, slowing resin oxidation and preventing rapid resin heatup due to heat release of oxidation reactions. This hypothesis was tested by prewetting the XAD-2 sorbent in the next sample train with organic-free water (about 200 ml) prior to sample collection. The sample rate was also reduced until a flow of condensate over the XAD-2 was occurring (about 10 minutes). Thereafter the sample rate was increased to the isokinetic sample rate for the duration of the sample period. These steps prevented noticeable resin charring or decomposition. Because of this success, the XAD-2 and Tenax resins were prewetted prior to sample collection for all Method 0010, 0023A, 0030, and 0031 trains.

Other sampling modifications that resulted from the Presurvey tests included (a) a reduction in sample volume for the Method 0060 trains to prevent depletion of the KMnO₄ Hg adsorbing solution, and (b) insulation of the condenser to further improve offgas cooling at the XAD-2 cartridge inlet.

Following the Presurvey (and following each successive test series), a post-job briefing was conducted. The post-job briefing identified any technical, safety, or other deficiencies. Corrective actions were implemented to address these deficiencies. This ensured that all safety hazards were identified and that engineering and administrative barriers were adequate for safely performing the sampling activities. Once low radiological contamination levels were verified, one XAD-2 cartridge from a Method 0010 train and one pair of VOST tubes were shipped to the analytical laboratory to determine if the samples could be successfully analyzed. The results affirmed the possibility of obtaining valid results even when the offgas was not diluted. The decision was made to conduct most of the subsequent sampling without diluting the sample gas.

Test Series 1 was performed after the Presurvey and post-job briefing provided assurance that the testing can be safely performed and that the offgas samples can be obtained, shipped to the analytical laboratory, and analyzed. Test Series 1 was the first of three test series. This test series was a dry run for the full scope of the field testing, sample handling, and sample analysis. The Calciner was operated under nominally the same conditions as the Presurvey. The Calciner operating temperature was 500 C. No sample gas dilution was done except for SVOC and PAH sample trains, that were run with and without sample gas dilution. Results of these trains will provide additional information regarding the value of sample gas dilution to lower NO_x levels.

Test Series 2 was a planned repeat of Test Series 1, to be conducted following any corrective actions identified in Test Series 1. Test Series 2 was expected to provide the highest quality and most acceptable data for the nominal 500°C Calciner operating temperature. There were a few variations in Test Series 2 from Test Series 1:

- Replacement of Method 0030 with Method 0031 (Sampling Method for Volatile Organic Compounds or SMVOC), to improve the capability to quantify emissions of VOCs with boiling points less than 30 C. There was insufficient time in the schedule to include Method 0031 testing prior to Test Series 2.
- Exclusion of any sample train dilution, on the basis of the preliminary indication from the Presurvey and Test Series 1 that undiluted NO_x interference was within acceptable limits.

- Refinements were made in the post-test XAD-2 and Tenax rinsing and recovered solution neutralization procedures
- TO-14 (VOC sampling and analysis using Summa canisters) was added to better evaluate VOCs without the potential interference of organic degradation products from NO_x and Tenax interactions
- The Teflon-lined VOST probe was replaced with a glass-lined VOST probe

Test Series 3 was conducted to evaluate test procedures and Calciner emissions when the Calciner was operated at 600°C. Calciner operation at this higher temperature can enable faster waste treatment with less additives that add to the calcine product mass. The scope of testing used in Test Series 2 was repeated in Test Series 3, with the following variations:

- Separate Method 0060 sample trains were performed for collecting metals excluding Hg, and metals including Hg. The non-Hg sample trains were run without the acidified KMnO₄ impingers to eliminate any interference from the Mn in the KMnO₄ on Mn analysis, and to increase the sample volume (which was limited when Hg collection was included to prevent depleting the KMnO₄ solution) to improve detection limits for the non-Hg metals.
- Analysis of coplanar PCBs was added to the D/F and total PCB analyses for the 0023A sample trains
- Temperature-controlled, heated insulated containers were used to keep the 0040 bags warm between sample collection and sample analysis to prevent potential loss of analytes through adsorption onto the bag walls.
- Glass-lined Summa canisters instead of unlined canisters were used for the TO-14 VOC sample collection
- Additional refinements were made in the post-test XAD-2 and Tenax rinsing and recovered solution neutralization procedures

Calciner System Operating Conditions

The Calciner was operated under nominally stable and normal conditions during each test. Important Calciner system operating conditions including flowrates, pressures, and temperatures are monitored, controlled, and recorded using a Distributed Control System (DCS). The waste feedrate was reduced from a typically higher feedrate of around 180 gal/hr to around 160 gal/hr, because this lower feedrate range can be more easily maintained even if one of the waste feed nozzles fails during operation. The lower feedrate also increased the batch time for each feed tank from 12-15 hours to up to 20 hours, further enhancing stable operation. Occasionally, process upsets such as feed nozzle plugging, variations in fluidized bed performance, or HEPA filter pressure drop changes occurred. Also, some maintenance activities such as HEPA filter change-outs and filter washing, as well as minor adjustments in offgas system operating temperatures, was done. These kinds of process upsets and maintenance are routine. When they occurred, and if operating conditions varied outside of desired ranges, then sample collection was interrupted until operating conditions were restored within acceptable ranges.

RESULTS, CONCLUSIONS & PLANS

Sample analysis, data reduction, and data evaluations for the emissions inventory tests are presently in progress. Emission measurements have not yet been reviewed for data quality, nor released for external reporting. Even though emissions data are not yet released for external reporting, the preliminary results show that standard offgas sampling and analysis procedures have been successfully adapted for and used to safely measure offgas emissions from a process that calcines highly radioactive liquid mixed wastes. The test program resulted in (a) test method adaptations to minimize NO_x interference during sampling and analysis, (b) development of procedures to mitigate radioactivity and industrial hygiene hazards during all phases of sample collection, sample shipping, and analysis, and (c) unprecedented measurements of offgas emissions from the Calciner process. Safety analyses,

technical procedures for sampling and sample handling, offgas containment strategies and equipment, and safe work techniques that were necessary to safely sample offgas from this process that treats highly radioactive process were developed and implemented. Several adaptations to improve data quality were also identified and evaluated in bench, pilot, or field tests. Although sample collection was encumbered by controls that protected against worker exposure or environmental release of radioactive contamination and dangerous levels of hazardous or toxic materials, the sample collectors soon developed skill and efficiency in setting up and leak-checking the trains and collecting and recovering the samples inside the contamination hoods.

Preliminary emission results have been sufficient to validate the calculations used in the site-specific screening level risk assessment, and confirm the risk assessment conclusion that risks from Calcliner operations are within acceptable limits.

The success of this project has been due to the technical reviews and inputs by the NTW-sponsored workgroup and through the coordinated efforts of the multidisciplinary project team.

Continued Calcliner offgas testing is planned during 1999 and early 2000 to provide additional emissions measurements while the Calcliner is operated at high temperature (600°C), better evaluate the emissions of some specific compounds that may improve Calcliner system mass balances or may be risk drivers, expand the emissions inventory to include some compounds not already measured, and evaluate emissions over a range of Calcliner system operating conditions that would represent bounding operating conditions.

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